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## An overview of ISCAT 2000

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### Abstract

The Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) took place over the time period of 15 November to 31 December in the year 2000. The study location was the Amundsen Scott Station in Antarctica. ISCAT 2000 defines the second phase of a program designed to explore tropospheric chemistry in Antarctica. As in 1998, the 2000 ISCAT study revealed a strong oxidizing environment at South Pole (SP). During the 2000 investigation, however, the suite of measurements was greatly expanded. These new measurements established the recycling of reactive nitrogen as a critical component of this unique environment. This paper first presents the historical background leading up to the ISCAT 2000 observations; then it focuses on providing a summary of the year 2000 results and contrasts these with those recorded during 1998. Important developments made during the 2000 study included the recording of SP data for several species being emitted from the snowpack. These included NO, H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O. In this context, eddy-diffusion flux measurements provided the first quantitative estimates of the SP NO and NO<sub>x</sub> snow-to-atmosphere fluxes. This study also revealed that HNO<sub>3</sub> and HO<sub>2</sub>NO<sub>2</sub> were major sink species for HO<sub>x</sub> and NO<sub>x</sub> radicals. And, it identified the critical factors responsible for SP NO levels exceeding those at other polar sites by nearly an order of magnitude.

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Finally, it reports on the levels of gas phase sulfur species and provides evidence indicating that the absence of DMS at SP is most likely due to its greatly shortened chemical lifetime in the near vicinity of the plateau. It is proposed that this is due to the influence of NO on the distribution of OH in the lower free troposphere over a region that extends well beyond the plateau itself. Details related to each of the above findings plus others can be found in the 11 accompanying Special Issue papers.

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## 1. Introduction

### 1.1. Pre-ISCAT results

As stated in a 1991 symposium on Antarctic Tropospheric Chemistry, “there are many unique features of Antarctica that make it a valuable laboratory for monitoring and understanding the state of our global environment” (Bodhaine et al., 1992). Clearly, one of the most unique features of this land of ice is that it represents a giant archive of atmospheric conditions dating back nearly 500,000 years bp (Legrand and Feniet-Saigne, 1988; Legrand et al., 1991, and references therein). Thus, all major global geophysical, biological, and/or climatological events that have had a measurable impact on atmospheric composition are recorded in some form in the vast ice accumulations on this continent. However, for a species’ ice signature to be of real scientific value one must have a reasonably good understanding of what the major atmospheric sources of the species are. This critical information has in some cases already been generated from past Antarctic studies. In other cases it is being produced by on-going studies such as the current one.

Sulfur is one of the elements found in ice cores that has been previously studied in the Antarctic atmosphere. In fact, some of the earliest studies involving this element have shown that it is one of the major elements to be found in aerosol samples (Shaw, 1980, 1988, and references therein). During the summer months, it is the dominant element. Because of this, sulfur has become a critical proxy species used to identify major global geophysical events such as volcanic eruptions and El Niño occurrences (e.g., Legrand and Delmas, 1987; Bergin et al., 1998; Dibb and Whitlow, 1996). However, based on results showing that most sulfur reaching the mainland is a by-product of locally released marine dimethyl sulfide (DMS), fluctuations in the levels of the oxidation products from DMS can also be used as climate proxy species (Legrand and Saigne, 1988; Legrand and Feniet-Saigne, 1991; Legrand et al., 1991; Legrand et al., 1992; Saigne et al., 1987; Mulvaney et al., 1992; Mulvaney and Wolff, 1994; Saltzman, 1994). Unfortunately, our knowledge about DMS oxidation chemistry is still quite limited. In addition, some of the

details concerning air-to-snow transfer processes for sulfur have been lacking (Bales and Wolff, 1995; Wolff and Bales, 1996; Davis et al., 1998).

Our lack of understanding of the mechanistic details about DMS oxidation can be illustrated here from a simple comparison of the sulfur oxidation products measured in aerosol samples collected at coastal sites versus those on the Antarctic plateau. Based on the known temperature dependencies for DMS oxidation via OH radicals (Hynes et al., 1986), arguments can be made that the ratio of the major products from DMS (i.e., methane sulfonate (MS) and non-sea-salt sulfate (NSS)) should be quite different for these two environments. The kinetic data, in fact, would suggest that the lower the average temperature the larger should be the value of this MS/NSS ratio. However, in spite of the much lower average temperature at the plateau, one typically finds that coastal values during the summer months are 3–10 times higher than those taken on the plateau (e.g., Saigne and Legrand, 1987; Prospero et al., 1991; Berresheim, 1987; Wagenbach, 1996; Arimoto et al., 2001; Legrand and Pasteur, 1998). Quite interestingly, the typical average plateau value for this ratio of 0.06 is a value that is consistently found for the tropical marine boundary layer (MBL) (Davis et al., 2003, and references therein). Even more confounding are observations at some coastal sites showing that at certain times the value of this ratio abruptly changes during the summer months, but with no corresponding temperature change (e.g., Prospero et al., 1991).

An earlier Georgia Tech/NCAR field initiative called Sulfur Chemistry in the Antarctic Troposphere Experiment (SCATE) provided considerable insight as related to the above observations. This program was focused on studying sulfur chemistry at Palmer Station on the Antarctic coast. Although this field study led to considerable speculation about the specifics concerning DMS oxidation, the larger picture emerging from it revealed that an estimated half of the total available surface released DMS (near Palmer) underwent oxidation at high altitudes. Evidence supporting this conclusion was found in the form of direct measurements of the intermediate DMS oxidation product, dimethylsulf-oxide (DMSO) (Berresheim et al., 1998). Laboratory kinetic studies have shown that under low temperature

conditions the dominant initial DMS oxidation product is DMSO (Barnes et al., 1996; Sørensen et al., 1996; Hynes et al., 1986). However, during SCATE, the levels of this species, as well as the byproduct from the further oxidation of DMSO (e.g., dimethyl sulfone (DMSO<sub>2</sub>)), were found to be highly variable, at times changing by factors of 10 or more over a period of just a few hours. Quite significant also was the finding that given the measured levels of DMS and hydroxyl radical (OH), it was not possible to explain the observed high concentrations of DMSO (Davis et al., 1998). Further analysis, in fact, revealed that these abrupt increases in DMSO correlated with air parcels descending from higher altitudes, e.g., depressed dew points and aerosol levels with elevated O<sub>3</sub> levels (Davis et al., 1998). Legrand et al. (2001) in a study at Dumont Urville found somewhat similar results, observing sudden unpredictable elevated levels of DMSO and DMSO<sub>2</sub>.

The SCATE study was also revealing in that it strongly suggested that a very large fraction of the DMSO that was returned to the MBL was rather efficiently converted into MS via heterogeneous processes involving sea-salt aerosols (Jefferson et al., 1998). Collectively, these results led to the tentative conclusion that the low MS/NSS ratio found on the plateau most likely was a result of the high-altitude oxidation of the intermediate, DMSO. Specifically, it required that DMSO be further oxidized under conditions involving very low temperatures and very low sea-salt levels (D. Davis, paper in preparation). As discussed by Arimoto et al. (2001), an examination of the MS/NSS ratio at different polar sites reveals that it is the MS level, not NSS that undergoes major shifts in concentration. As noted above, within the MBL DMSO predominantly disappears via heterogeneous reactions involving sea-salt to form MS; while at higher altitudes, free of sea-salt, the dominant reaction of DMSO can involve reaction with OH, leading to SO<sub>2</sub> formation and subsequently to NSS (D. Davis, paper in preparation).

Based on the above hypothesis, a new research initiative was formulated which focused on making detailed observations of sulfur species at the South Pole (SP). The argument put forward for this new sampling strategy was as follows. During those time periods when coastal marine air moved rapidly inland and reached the SP in 2–3 days, considerable amounts of un-reacted DMS would be delivered to the SP site. Under these conditions, the SP setting could thus provide an excellent opportunity to monitor the entire chemical evolution of DMS under very low temperature and salt-free conditions.

The resulting new sulfur chemistry initiative, Investigation of Sulfur Chemistry in Antarctica Troposphere (ISCAT) focused on two major objectives: (1) assessing the relative importance of the atmospheric chemical, physical, and meteorological factors responsible for

defining gas and aerosol phase sulfur speciation at SP; and (2) evaluating the role of H<sub>2</sub>SO<sub>4</sub>, MSA, H<sub>2</sub>O, NH<sub>3</sub>, and temperature in the formation and growth of new particles under SP conditions. A secondary ISCAT objective involved examining the key factors modulating the atmospheric oxidizing power (e.g., OH levels) at SP. Recall, it is the level of OH that controls the rate of oxidation of any DMS transported to SP.

### 1.2. ISCAT 1998 results

Among the major findings from ISCAT 1998 was the observation that DMS levels were typically at or below the detection limit of our instrumentation, e.g., <2 pptv. These low values of DMS were reflected in the equally low values observed for the oxidation products MSA and H<sub>2</sub>SO<sub>4</sub> (Mauldin et al., 2001). Even so, the ISCAT 1998 sulfur aerosol results demonstrated for the first time that the value of the airborne aerosol MS/NSS ratio (i.e., 0.07) was indistinguishable (within the uncertainties of the analyses) from the average value typically cited for near surface ice cores from the plateau (Arimoto et al., 2001). Thus, these results would suggest that what actually reaches the plateau in the form of aerosol is what gets deposited. It is likely then that this ratio is the end result of pre-plateau chemical/dynamical processes that take place during transport.

The reason for the very low DMS levels at SP will be addressed later in the text as well as in two of the accompanying papers in this Special Issue. Taken at face value, however, they suggest that either our original estimate of the transport time for DMS from the coast to SP was too short or that the average oxidation rate via OH was much faster than first calculated.

Without question, the most surprising finding during the 1998 study was observing the photodenitrification of surface snow as the major source of atmospheric NO<sub>x</sub> at SP (Davis et al., 2001). In this regard, it is noteworthy that similar findings were also independently recorded at Alert, Canada (Ridley et al., 2000), at Summit, Greenland (Honrath et al., 1999) and at Neumayer on the coast of Antarctica (Jones et al., 2000). What makes the 1998 ISCAT NO results so exceptional is the magnitude of the NO concentration. As summarized in Davis et al., 2004, the median 1998 level of 225 pptv is nearly a factor of 10 greater than at other polar sites, including those recorded at two coastal Antarctica locations. One of the major chemical consequences resulting from such high levels of NO is its impact on the levels of OH (Davis et al., 2001). Reflecting this fact, the ISCAT 1998 data resulted in an estimated 24 h average value for OH of  $\sim 2 \times 10^6 \text{ mol cm}^{-3}$ . This places the oxidizing power of near surface air at SP as equal to or slightly exceeding that of the tropical marine BL (Mauldin et al., 2001). (Note, the latter environment has traditionally been viewed as having one of the highest average OH levels

for a remote site.) This level is nearly 10 times larger than any previous model prediction for this region. However, all previous predictions have been based on NO levels similar to that measured at Palmer Station during the SCATE program, e.g.,  $\leq 5$  pptv (Chen et al., 2001).

## 2. ISCAT 2000 site location and instrumental techniques

Given the cited  $\text{NO}_x/\text{HO}_x/\text{O}_3$  and DMS/sulfur surprises of ISCAT 1998, there was a major reconfiguring of the ISCAT 2000 field study. Its new focus was shifted to  $\text{NO}_x/\text{HO}_x$  science issues. Key objectives included: (1) establishing the chemical characteristics of the SP snowpack (e.g.,  $\text{NO}_3$ -levels) relative to the surrounding terrain; (2) assessing the magnitude of the  $\text{NO}_x$  emission flux; (3) evaluating the possible contributions of other snowpack trace gas emissions (e.g.,  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , and HONO) on the budgets of  $\text{HO}_x$  and  $\text{NO}_x$ ; (4) reassessing the factors responsible for the large day to day shifts observed in  $\text{NO}_x$  levels; (5) evaluating the major sinks for  $\text{NO}_x$  and  $\text{HO}_x$  (e.g.,  $\text{HNO}_3$ ,  $\text{HO}_2\text{NO}_2$ ); and (6) exploring the relationship between synoptic conditions and the efficiency with which gas phase sulfur species get transported to SP.

In addition to the new objectives for ISCAT 2000 cited above, there was also the important task of contrasting the results from the 1998 ISCAT study with those from 2000. As covered in the 11 papers in this Special Issue, significant differences were found between the two. This paper notes these differences, and the accompanying 11 papers will examine in greater detail some of the reasons behind the differences.

### 2.1. Site location

The major sampling site during ISCAT 2000 was the Atmospheric Research Observatory (ARO) building at SP. More limited sampling took place on the SP MET tower and from several surface sites, most of which were relatively close to the ARO building (e.g., 50 m). The farthest distance at which sampling occurred was a snow pit  $\sim 12$  km from ARO. As noted in earlier ISCAT papers (Davis et al., 2001 and adjoining papers), the ARO building at SP is positioned at the apex of what is known as the “clean air sector”. This sector is nominally defined as  $0$ – $120^\circ$ . It is therefore upwind of the main SP dome and all power generating facilities. Equally important, the dominant wind direction ( $80$ – $90\%$ ) falls within this sector. Thus, it encompasses the major flow coming off of the polar plateau (labeled downslope flow). The latter defines the coldest/driest air that can be sampled at SP. By contrast, wind directions in the range  $330$ – $180^\circ$  have been labeled as upslope flow and typically lead to an inflow of warm/moist air of marine

origin. The chemical differences in these air masses is amplified on in three papers in the ISCAT 2000 Special Issue (e.g., see Davis et al., 2004; Swanson et al., 2004; Arimoto et al., 2004a, b).

### 2.2. Instrumental techniques

Virtually all of the measurements recorded during the 1998 campaign were repeated during ISCAT 2000. Many new measurements, however, were added in 2000. Table 1 provides a summary of the ISCAT 2000 measurements. Included here are the principle investigator, the instrument's sensitivity, and what years it was used. Further details concerning each technique can be found either in the individual ISCAT papers appearing in this Special Issue or in the Special ISCAT Section of Geophysical Research Letters Vol #19 in October of 2001.

## 3. Overview of meteorological observations

### 3.1. Average and median meteorological conditions during ISCAT 1998 versus ISCAT 2000

In the text that follows, the ISCAT 1998 and 2000 studies are both examined individually and contrasted. As seen in Table 2, some of the seasonal MET trends in 1998 are what one might expect, given the intensity of the seasonal changes at SP. The temperature, for example, undergoes a major increase from late November to early December but then levels out. A similar trend is also seen in the dew point. In contrast, the median value for atmospheric barometric pressure is nearly constant from the middle of November to the middle of December, then increases during the last half of December. The wind speed, on the other hand, shows the reverse trend, systematically decreasing across the entire sampling time period. By contrast, the trend in the temperature gradient, as measured as the difference between 22 and 1.6 m on the MET tower ( $\Delta T$ ), shows almost no trend during the 1998 sampling season, all values lying within  $0.3^\circ$  and positive.

The ISCAT 2000 MET data reveals some significant deviations from those recorded in 1998. However, one trend that was similar in both years was wind speed. As in 1998 a systematic decrease is evident in the 2000 data from the last half of November to the last half of December. The 1998 temperature and dew point data, on the other hand, are seen as systematically lower than those in 2000. In November the difference was nearly  $5^\circ$ , but by the end of December it had decreased to only  $1^\circ$ . The 2000  $\Delta T$  values go from small positive values in late November and the first-half of December to small negative values in late December, again quite different from the trend that one sees in the ISCAT 1998 data. Barometric pressure levels during the 2000 field study

Table 1  
ISCAT 2000 atmospheric measurements

Compound	Investigator	Technique	Sensitivity	Meas. 1998
HNO <sub>3</sub>	Huey	SICIMS	5 pptv	New 2000
	Dibb	Mist chamber/IC	1 pptv	New 2000
HO <sub>2</sub> NO <sub>2</sub>	Huey	SICIMS	5 pptv	New 2000
SO <sub>2</sub>	Bandy	CIMS	1–2 pptv	New 2000
	Huey	CIMS	(a)	New 2000
CH <sub>2</sub> O	Hutterli	Scrubber/Fluorescence	30 pptv	New 2000/
		Spectroscopy		Collaborative
HONO	Dibb	Mist chamber/IC	1 pptv	New 2000
H <sub>2</sub> O <sub>2</sub>	Hutterli	Scrubber/Fluorescence	50 pptv	New 2000/
		Spectroscopy		collaborative
OH	Eisele	SICIMS	$1 \times 10^5 \text{ mol cm}^{-3}$	Yes
HO <sub>2</sub> /RO <sub>2</sub>	Eisele	SICIMS	$5 \times 10^5 \text{ mol cm}^{-3}$	New 2000
H <sub>2</sub> SO <sub>4</sub>	Eisele	SICIMS	$1 \times 10^5 \text{ mol cm}^{-3}$	Yes
MSA	Eisele	SICIMS	$1 \times 10^5 \text{ mol cm}^{-3}$	Yes
NMHC and Halocarbons	Blake	Grab sample/GC and GC/MS	0.05–5 pptv	Yes
DMS	Blake	Grab sample/GC/MS	1 pptv	Yes
	Bandy	CIMS	1–10 pptv	Yes
DMS	Bingemer	Goldwool/Fluorescence	1–2 pptv	Yes
Actinic flux	Shetter	Spectroradiometer	N/A	Yes
NO	Davis/Buhr	Chemiluminescence	2 pptv	Yes
HCO <sub>2</sub> H and CH <sub>3</sub> CO <sub>2</sub> H	Dibb	Mist chamber/IC	1 pptv	New 2000
Aerosol size and number	McMurry	CNC, UFCNC, OPS	$0.01 \text{ cm}^{-3}$	Yes
O <sub>3</sub> , Temp, DP, Pressure, wind, speed/direction, Col. O <sub>3</sub> , Solar Irradiance	CMDL-South Pole Station	Multiple Techniques Irradiance-Biospherical Inst.	Suitable for South Pole	Yes collaborative
NO Flux	Oncley/Davis	Sonic anemometers/Chemiluminescence		New 2000
Aerosol ion comp. and gas phase HNO <sub>3</sub>	Arimoto	IC	$30 \text{ ng m}^{-3}$	Yes
Aerosol elemental composition	Arimoto	ICP-MS, AAS, Gamma Spectrometer	$30 \text{ ng m}^{-3}$	Yes
Measurements in the snow made during ISCAT 2000				
NO	Davis	Chemiluminescence	2 pptv	New 2000
NO <sub>2</sub>	Huey	SICIMS	100 pptv?	New 2000
CH <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub>	Hutterli	Scrubber/Fluorescence	40 pptv	New 2000
Snow ion composition	Dibb	IC	Variable	New 2000

also differed somewhat from 1998 as revealed in Table 2 in the form of median values for each 15 day sampling time-period. Although the differences in several of the individual MET variables appear to be quite modest between the two sampling years, as discussed below they seem to reflect rather major differences in the synoptic conditions for the two years.

### 3.2. Brief synoptic overview

A common meteorological condition on the Antarctic plateau involves cold continental surface air flowing past

the SP after several days of residence on the plateau itself. Even so, the presence of a pressure gradient about one or more low-pressure centers, usually over the Ross Sea/Shelf or the Weddell Sea, can induce warmer “extra-continental” air to flow over the SP from western hemispheric directions. This warm inflow can occur several times in November, but influences only a few days in December and January. During ISCAT 2000, there was also observed an inflow of “extra-Antarctic” air (i.e., air beyond the Antarctic Convergence-60°S) associated with a high-pressure ridge that developed during the break-up of the polar vortex. These three





stagnation period which followed the filling of the polar vortex had a residence time over the snow of more than five days, and residence times up to 10 days, e.g., 4–14 December 2000, occurred at that time. Later in December 2000, occasional inflows to SP, resulting from flow around the weak low-pressure center forming over the Ross Ice Shelf, were also shown from air trajectory analysis to have much shorter residence times.

#### 4. Overview of chemical species measurements

##### 4.1. Average and median levels of gas phase species during ISCAT 1998 versus ISCAT 2000

As shown in Table 3 only six gas phase species were extensively measured in both years, and thus, the focus here will be on these, e.g., NO, O<sub>3</sub>, CO, H<sub>2</sub>SO<sub>4</sub>, MSA, and OH. Of the six trace gases listed, it is quite apparent that NO underwent one of the largest changes between field studies. In 1998 the median value was in the 200–250 pptv range for the month of December. In contrast, for the last half of November 2000, the median NO was 93 pptv, and dropped into the eighties during December. Extreme variations in the day to day values of NO are apparent in the very large standard deviations cited for the mean values of NO, both for 1998 and 2000.

Median O<sub>3</sub> levels in 1998 underwent a very modest decrease from the last half of November to the last half of December; whereas, in 2000 there was some meandering in the levels observed, with the maximum value in the median occurring in the first half of December. However, the medians for both years tended to range from 30 to 35 ppbv; and as seen in Table 3, mean values were typically within 1 ppbv of the median. One of the more interesting characteristics of the O<sub>3</sub> data is the rather large standard deviation cited in both the 1998 and 2000 data. As noted by Crawford et al. (2001), this large value primarily reflects the major oscillations that can occur in SP O<sub>3</sub> levels over the course of just a few days due to the net photochemical formation of this species. The positive excursions in O<sub>3</sub> above the median value typically exceed the well-documented maximum in O<sub>3</sub> that occurs during the Austral winter season.

The trend in median CO is similar to that for O<sub>3</sub> in that CO is seen decreasing from the second half of November to the last half of December. This decrease reflects the enhancement in CO's photochemical destruction as driven by its oxidation via reaction with OH. However, the difference between sampling years is seen as being quite modest with the final values in the last half of December for both studies being nearly identical. Only in the second half of November is there a significant difference in CO levels, the median value for 1998 being 3 ppbv higher than in 2000.

Table 3

Median and mean values for gas phase chemical species and photochemical parameters for ISCAT 1998 and 2000

	Nov. 15–30				Dec. 1–15				Dec. 15–31			
	1998		2000		1998		2000		1998		2000	
	Avg.	Med.	Avg.	Med.	Avg.	Med.	Avg.	Med.	Avg.	Med.	Avg.	Med.
$J(\text{O}^1\text{D}) (\text{S}^{-1}) \times 10^{-6}$			5.9 ± 1.8	5.3	8.2 ± 0.5	8.16	6.7 ± 0.7	6.8	8.6 ± 1.3	8.9	8.5 ± 0.8	8.5
$J(\text{NO}_2) (\text{S}^{-1}) \times 10^{-2}$			0.88 ± 0.15	0.91	1.1 ± 0.1	1.0	1.0 ± 0.1	1.1	0.95 ± 0.11	1.0	1.0 ± 0.1	1.1
NO (pptv)			102 ± 69	93.379	214 ± 84	209	95 ± 103	82.	244 ± 120	237	113 ± 102	88
O <sub>3</sub> (ppbv)	34.4 ± 5.3	35.1	32.2 ± 3.4	32.3	32.6 ± 5.9	32.6	35.6 ± 3.1	35.2	27.7 ± 7.0	26.1	29.3 ± 5.8	30.0
CO (ppbv)	45.1	44.2	40.1 ± 1.6	40.0	37.7		37.4 ± 2.0	37	34.5		34.3 ± 2.7	34.35
C <sub>2</sub> H <sub>6</sub> (pptv)			215 ± 12	214	439 ± 186	417	181 ± 26	180	383 ± 153	376	144 ± 13.6	145
CH <sub>2</sub> O (pptv)							109 ± 36	122			100 ± 29	105
H <sub>2</sub> O <sub>2</sub> (pptv)							288 ± 129	294			231 ± 74	229
OH (m cm <sup>-3</sup> ) × 10 <sup>6</sup>			2.5 ± 0.6	2.4	1.6 ± 0.4	1.4	2.6 ± 1.0	2.9	1.9 ± 1.1	1.7	2.1 ± 0.8	2.3
PO <sub>2</sub> (m cm <sup>-3</sup> ) × 10 <sup>7</sup>											8.3 ± 2.4	8.1
HCO <sub>2</sub> H (pptv)							70 ± 42	58			124 ± 83	85
CH <sub>3</sub> CO <sub>2</sub> H (pptv)							231 ± 126	215			275 ± 119	264
HONO (pptv)							8.0 ± 3.7	7			27.0 ± 7.4	28
HNO <sub>3</sub> UNH (pptv)							35.3 ± 8.4	33.8			23.5 ± 11.4	19.9
HNO <sub>3</sub> GT (pptv)											19.3 ± 11.4	18.2
HO <sub>2</sub> NO <sub>2</sub> (pptv)											23.3 ± 10.9	23.5
DMS (pptv)					<2	<2	6.6 ± 5.3	3.3	1.7 ± 3.9	0.7	1.9 ± 1.0	1.4
SO <sub>2</sub> (pptv)			7.8 ± 4.6	6.5			9.9 ± 11.4	4.5			5.7 ± 4.3	2.8
H <sub>2</sub> SO <sub>4</sub> (m cm <sup>-3</sup> ) × 10 <sup>5</sup>			2.9 ± 1.2	2.9	2.5 ± 0.3	2.5	3.0 ± 1.3	3.0	2.5 ± 1.5	2.4	2.4 ± 1.4	2.3
MSA (m cm <sup>-3</sup> ) × 10 <sup>4</sup>			5.3 ± 3.2	4.81	5.9 ± 2.8	5.6	5.9 ± 6.3	4.4	7.5 ± 12	4.6	6.9 ± 8.2	3.8



For the shorter lived species OH, H<sub>2</sub>SO<sub>4</sub>, and MSA, the trends within a given sampling season are very weak and lie clearly within the standard deviations cited in Table 3. In the case of H<sub>2</sub>SO<sub>4</sub> and MSA, there is only a very modest difference between the 1998 and 2000 seasons, e.g., they fall well within the stated uncertainties. Only in the case of OH can one possibly make an argument that perhaps the 2000 data are systematically higher. However, given the large uncertainty assigned to the calibration of the OH SICIMS system in 1998, it is difficult to argue that a major difference exists between the two sampling seasons. As stated by Mauldin et al. (2001), what is apparent is that the oxidizing power at the SP rivals or exceeds that in the tropics (i.e., the tropical marine BL) based on both year's sampling.

#### 4.2. Median and mean values of radiative parameters

Both the values of  $J(\text{NO}_2)$  and  $J(\text{O}^1\text{D})$  are shown in Table 3 increasing as the observational period moved from mid-November to the end of December. However, the degree of change for  $J(\text{NO}_2)$  is seen as quite modest, reflecting the much larger dependence of this “ $J$ ” value on longer wavelength radiation. By contrast,  $J(\text{O}^1\text{D})$  is strongly dependent on low wavelength UV radiation, making it sensitive to both the solar path-length and the overhead O<sub>3</sub> column density. Thus, significant variations in its value can occur during the spring/summer season. This is revealed in Table 3, where it can be seen that a significant shift in the value of  $J(\text{O}^1\text{D})$  occurred over the course of the 2000 study, and a significant difference can also be seen between the 1998 and 2000 values for the same time of year due to 1998 having a lower overhead O<sub>3</sub> column density in early December. (For additional detail the reader is directed to Lefer et al. (2001).)

#### 4.3. Median and mean values for aerosol species

Of the aerosol species shown in Table 4, NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, and MS were the three species for which data were collected in both the 1998 and 2000 studies. For both NO<sub>3</sub><sup>−</sup> and SO<sub>4</sub><sup>2−</sup> no major trend can be seen within the years 1998 or 2000 during the sampling season itself. But, this is not true for MS which in 2000 decreased by over a factor of 2 from the second half of November to the first half of December. In contrast, no significant trend is seen in the 1998 data over the month of December. By far the most important trend in these aerosol data is the difference seen when comparing the 1998 with the 2000 results. For example, the 1998 SO<sub>4</sub><sup>2−</sup> values are typically a factor of 2 higher and MS levels are at least a factor of 4 higher. Interestingly, NO<sub>3</sub><sup>−</sup> shows just the opposite trend, with 2000 levels being approximately 4 times higher than those in 1998. (For further details see Arimoto et al. (2001).)

Table 4  
Median and mean values for aerosol species for ISCAT 1998 and 2000

	Nov. 15–30		Dec. 1–15		Dec. 15–31	
	1998		1998		2000	
	Avg.	Med.	Avg.	Med.	Avg.	Med.
Na <sup>+</sup> (μg m <sup>−3</sup> )			0.047±0.021	0.042	0.035±0.018	0.030
NO <sub>3</sub> <sup>−</sup> (μg m <sup>−3</sup> )		0.14	0.041±0.018	0.045	0.038±0.024	0.032
SO <sub>4</sub> <sup>2−</sup> (μg m <sup>−3</sup> )	0.13±0.06	0.104	0.21±0.05	0.20	0.22±0.05	0.21
MS (μg m <sup>−3</sup> )	0.11±0.02	7.0	11.8±4.7	10.4	11.3±4.1	11.6
Be <sup>7</sup> (fCi m <sup>−3</sup> )	6.5±2.8	LOD	205±90	174	157±28	148.5
Pb <sup>210</sup> (fCi m <sup>−3</sup> )	LOD	LOD	LOD	LOD	LOD	LOD
Hg (ng m <sup>−3</sup> )	0.19±0.11	0.18		0.20±0.16	0.15±0.04	0.086±0.041
				0.22	0.10±0.02	0.079
					4.6±3.5	3.1
					LOD	LOD
					LOD	LOD

## 5. Research highlights—ISCAT special issue papers

### 5.1. $\text{HO}_x/\text{NO}_x/\text{O}_3$ and fast photochemistry

It is now quite apparent that the ISCAT 2000 field study has moved our understanding of SP photochemistry substantially forward relative to where we were at the end of ISCAT 1998. At the end of the 1998 study, there was speculation that other  $\text{HO}_x$  sources might be present at SP (Chen et al., 2001). The  $\text{H}_2\text{O}_2$  and  $\text{CH}_2\text{O}$  observations during ICAT 2000 have now made quite evident that this is almost certainly true (see e.g., Chen et al., 2004; Hutterli et al., 2004). For example, the new observations have shown that even though generated photochemically in the gas phase, a still larger source of these species exists in the form of emissions from the snowpack (Hutterli et al., 2004). The reporting of the first of their kind measurements of the radical species ( $\text{HO}_2 + \text{RO}_2$ ), has also resulted in a more rigorous testing of current photochemical mechanisms (e.g., Mauldin et al., 2004; Chen et al., 2004). A major surprise arising from the ISCAT 2000 observations was finding relatively high levels of HONO. Using the observed concentration values for this species dramatically altered the predicted levels of OH. They also lead to the conclusion that HONO emissions could be the major source of atmospheric  $\text{NO}_x$  (Dibb et al., 2004; Chen et al., 2004). This result, therefore, has raised yet a new set of questions related to possible missing sinks for  $\text{HO}_x$  and  $\text{NO}_x$  or alternatively, problems with the HONO measurement itself.

The field measurements of NO during 2000, both within the snowpack and in the atmosphere at multiple elevations, have confirmed the credibility of the 1998 observations and clearly demonstrated that the source of  $\text{NO}_x$  is emission from the snow (Davis et al., 2004). The MET tower gradient measurements of NO, in conjunction with micro-MET observations of temperature, humidity, and wind speed, have also made possible the first flux estimates of NO and  $\text{NO}_x$  from surface snow at SP (Oncley et al., 2004). These values have been used to evaluate the recycling  $\text{NO}_x$  flux for the plateau and how this process might be influencing the distribution of near surface nitrate levels across the plateau (Davis et al., 2004). And finally, the detailed analysis of both the ISCAT 1998 and 2000 NO observations have been quite revealing in establishing the uniqueness of the SP site relative to other polar sites as related to  $\text{NO}_x$  levels. In particular, the fact that NO levels are nearly an order of magnitude higher at SP than at all other polar sites can now be understood in terms of the differences in 5 critical factors (e.g., see Davis et al., 2004).

Closely related to the above  $\text{NO}_x$  chemistry developments are the first of their kind SP measurements of  $\text{HNO}_3$  and  $\text{HO}_2\text{NO}_2$ . These new measurements performed during ISCAT 2000 have convincingly demon-

strated that the formation of these species define the dominate SP sinks for  $\text{HO}_x$  and  $\text{NO}_x$  (Huey et al., 2004; Slusher et al., 2002; Dibb et al., 2004). Equally interesting, and again related to the observed  $\text{HO}_x$  levels at SP and the intensity of photochemistry there, are the results involving marine emissions of the trace gases DMS,  $\text{CHBr}_3$ ,  $\text{CH}_3\text{I}$ , and  $\text{CH}_3\text{ONO}_2$ . These trace gases are removed from the atmosphere either via their oxidation via OH or by direct photolysis. Quite interestingly, the ISCAT 2000 results have convincingly shown that due to the wide range in chemical lifetimes, in conjunction with a wide range of possible transport times, quite different mixes of gases of marine origin can routinely arrive at SP even though the species start out at the same source location (e.g., see Swanson et al., 2004).

### 5.2. Aerosol and sulfur results

One of the surprising results of ISCAT 1998 was finding very little evidence of DMS and of  $\text{SO}_2$  at SP. This was also the case in the 2000 study (Swanson et al., 2004; Huey et al., 2004). The levels of  $\text{H}_2\text{SO}_4$  and MSA measured at SP in both years also tend to confirm that the source of sulfur aerosol is not due to the condensation of locally formed  $\text{H}_2\text{SO}_4$  and MSA (Mauldin et al., 2004; Park et al., 2004). However, the 2000 study did provide new evidence showing the coupling between  $\text{SO}_2$  and OH and the end product  $\text{H}_2\text{SO}_4$  (Huey et al., 2004). They also, with one possible exception, have provided evidence that conditions at SP are not, on average, favorable to the formation of new particle formation (Park et al., 2004). The one exception appears to be a case where the wind direction and low wind speed may have resulted in SP generator emissions influencing the observations at the ARO building. Quite significant as related to aerosol findings was also establishing that in both ISCAT 1998 and 2000 the median value for the ratio of MS/NSS was 0.07 (Arimoto et al., 2001). This observation has demonstrated for the first time that these two chemical species arrive at SP in approximately the same ratio as is typically found in plateau near-surface (1000 yr bp) ice cores (Saigne and Legrand, 1987). A final 2000 finding was observing for the first time at SP filterable Hg. The concentration levels found approached those reported in the Arctic; however, the chemical driving mechanism at SP appears to be quite different from that in the Arctic (Arimoto et al., 2004b).

### 5.3. Snow chemistry

A number of snow pits were examined during the ISCAT 2000 study in which the levels of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$ , were analyzed for comparison with earlier studies as well as comparison with studies at other polar sites in Antarctica and in Greenland (Dibb et al., 2004). Of particular interest here was the finding

that snowpits near the ARO building at SP did not contain appreciably different levels of  $\text{NO}_3^-$  as pits dug 12 km away. The levels of this species at SP also appear to be within a factor of 2–3 of other polar sites. In addition to the aforementioned ions, snow measurements were also recorded for the soluble species  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$  (Hutterli et al., 2004). In conjunction with gradient measurements from which flux values for these same species were estimated, ice modeling studies were carried out showing internal consistency between air and snow levels of these species (Hutterli et al., 2004).

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